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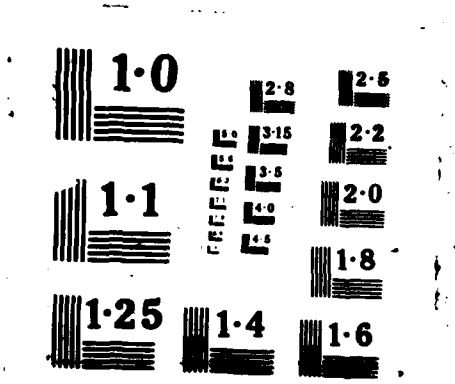
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Methods for the microcharacterization of solid state surfaces using the ion microprobe (SIMS) were investigated. Methods of obtaining quantitative depth and concentration information on multilayer thin film and interfaces were explored. In addition to superlattice quantification, in-situ ion implantation and examination of ion implantation damage were accomplished. SIMS ion yield variations for estimation of matrix effects were investigated. A cryogenic sample stage was designed and built for low temperature solid state studies on the ion microprobe. A study of spatial resolution of the ion microscope has resulted in extending the resolution from 500 nm to 100 nm. The technique of dark-field ion microscopy was developed for correlating surface relief with chemical contrast.

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# FINAL REPORT

SUMMARY OF PROGRESS DURING CONTRACT PERIOD (7/1/83 - 6/30/86)

## I. QUANTITATIVE MICROFEATURE ANALYSIS

### A. Superlattice Quantification

A method was developed for the analysis of $Al_xGa_{1-x}As$ by utilizing the observation that secondary ion yields and sputtering yields are linearly dependent upon sample matrix composition. Calibration lines for Be, Si, B, P, and As were obtained by use of practical ion yields, relative sensitivity factors, and relative ion yields. Calibration lines formed by using relative ion yields provided superior precision and accuracy (as demonstrated by superior line reproducability and linearity). Relative ion yield and sputtering yield calibration lines were applied to the determination of a B implant into a $GaAs/Ga_xAl_{1-x}As$ superlattice sample (4).

In an extension of the above work, a point-by-point matrix effect calibration was developed and applied to a variety of $Al_xGa_{1-x}As$ multilayer multimatrix structures grown by molecular beam epitaxy. The procedure employed uses the linear dependence of secondary ion yields and sputtering yields on matrix composition to quantify depth profiles through matrix gradients and interfaces. Through the use of these calibration lines the SIMS data were used to determine the matrix composition at each point through a gradient or interface which, in turn, was used to calculate trace element distributions through such structures. This method can provide accurate results in the analysis of samples far too complex for conventional quantitative analysis by secondary ion mass spectrometry (6).

Various explanations have been submitted for the variation of secondary ion and sputtering yields with matrix composition. Popular views include an inverse variation of relative ion yields to relative sputtering yields and the reported correlation between mean free energies of matrix-oxygen bonds and the observed trends in ionization probabilities. A study was conducted to investigate these two principal explanations using relative ion yield values from trace and major elements in various Group III-V compound matricies. A strong relationship between relative ion yields and relative sputtering yields was not observed. Alternatively, a very strong linear relationship was found between relative ion yield and the average bond energies in the sample matrix to oxygen. For elements in the same column of the periodic table, a direct correlation was observed between the slopes of these lines and the ionization potentials of the corresponding analytes. These trends were found to be informative in comparison to theory and in the prediction of the relative role of matrix effects in specific instances. Thus, the observed relationships can be used to improve the quality of both qualitative and quantitative SIMS analyses (8).

### B. In-Situ Ion Implantation and Examination of Ion Implantation Damage

The primary column of the CAMECA IMS-3f secondary ion mass spectrometer has been used as an ion implanter for the purpose of generating an internal standard into a semiconductor matrix. This technique extends the quantitative capabilities of the ion microanalyzer for depth-profile trace elemental analysis (12,16).

Methodology for successful analysis and quantification of heterogeneous or mixed matrix materials has been outlined for the case of biological materials by this research group (1). The procedure involves implanting the material of interest with a uniform dose of an element not present in the sample to serve as an internal standard.

SIMS has been used to study boron-doped Si[100] which was rendered amphorous by the implantation of $^{75}As$. Using oxygen bombardment and negative secondary ion detection, all secondary ion species show a shift in ion energy of greater than 2 ev upon sputtering through the amorphous layer and into the underlying crystalline silicon. After regrowth of the same specimens by rapid thermal annealing, the secondary ion energy shift occurs significantly deeper, at approximately the p-n junction. In both specimens, the energy shift was shown to be due to bombardment-induced specimen charging. This technique serves to extend the quantitative capabilities of the ion microanalyzer (22).

### C. SIMS Ion Yield Variations for Estimations of Matrix Effects in Quantification Schemes

Matrix effects on ionization probabilities have been investigated for ion imaging of plastic-embedded and ashed biological thin sections. Practical ion yield maps were constructed implanting Be as a reference element. These ion yield maps show variations in the Be signal on the order of a few percent. These results indicate that matrix effects are of relatively small importance in quantitative analyses of plastic-embedded and ashed (plastic embedded) samples (18,19).

## II. ION MICROSCOPY

### A. Instrumental Modification: A Cryogenic Sample Stage

Recently, a simple and inexpensive cold stage was developed for use with the CAMECA IMS-3f ion microscope (10). This system is readily adaptable to the existing equipment and is constructed of easily obtainable parts. The stage holds a sample specimen at -182°C with liquid nitrogen cooling. Data were obtained under cryogenic conditions for both biological specimens and the copper grid generally used for instrument alignment. This cold stage presents no more difficulty in operation than the standard stage on the ion microscope. In addition to biological studies, we are presently exploring other uses for this cold stage on our SIMS instrument such as ion mobility in the solid state at cryo temperatures and geological applications.

### B. Evaluation and Improvement of Lateral Resolution

Due to the variability in lateral resolution claims found in the literature and the desire to improve the imaging characteristics of the ion microscope, a critical evaluation of ion microscopic spatial resolution was performed. The lateral resolution obtained with the CAMECA instrument is generally quoted as between 0.3 and 0.1 μm. An accurate knowledge of the spatial resolution and the factors that influence it defines the scope of microfeature recognition as is necessary prior to image processing techniques. Standard test patterns were fabricated in the form of even square waves (or simple step function standards) using electron beam lithography/metallic evaporation and mask removal techniques. These were then imaged (via photographic methods) on the CAMECA IMS-3f ion microscope with subsequent digitization on a microdensitometer. These digitized images were analyzed, yielding signal traces gaussian in nature. Statistical tests were then used to evaluate the image resolution, which was found to be (at best) 0.53±0.03 μm. This important datum, along with the associated method, provides a thorough baseline with which the improvement of lateral resolution and image quality are facilitated (13).

To test the resolution-measuring technique mentioned above, the CAMECA IMS-3f ion microscope was temporarily modified with the intent of improving spatial resolution, followed by actual resolution measurement (15). Specifically, modifications have been presented for the CAMECA IMS-3f ion microprobe which extends instrumental

magnifications from 250X to 2200X, and smallest resolvable distances in undistorted images to 100 nm. This is necessary to keep pace with the increasingly stringent requirements for the analysis of shrinking features in fabricated VLSI devices. Conditions for ensuring the formation of undistorted images have been given, and the performance of the instrument under these conditions were evaluated (21).

C. Establishing the Dark-Field Ion Microscopic Technique

Dark-field images are observed with the stigmatic SIMS ion microscope (the CAMECA IMS-3f) by means of an eccentric contrast aperture, and are a useful extension of shadow contrast imaging, provided a narrow energy bandpass is selected to minimize chromatic aberrations. It has been demonstrated that the dark-field method is useful for correlating surface relief with chemical contrast in the compositional SIMS mapping of conventional ion microscopy. Further, based on the information acquired in the dark-field imaging mode, digital techniques to compensate for asperity artifacts in conventional ion microscopy have been proposed (20).

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Rept. No. 13 Oxide Bond Energies for the Calibration of Matrix Effects in Secondary Ion Mass Spectrometry - A.A. Galuska, G.H. Morrison, March 28, 1984.

Rept. No. 14 Cryogenic Sample Stage for the CAMECA IMS-3f Ion Microscope - M.T. Bernius, S. Chandra, G.H. Morrison, July 17, 1985.

Rept. No. 15 On-Line Implantation for Quantification in Secondary Ion Mass Spectrometry: Determination of Trace Carbon in Thin Layers of Silicon - H.E. Smith, G.H. Morrison, July 17, 1985.

Rept. No. 16 Evaluation of Ion Microscopic Spatial Resolution and Image Quality - M.T. Bernius, Y-C Ling, G.H. Morrison, September 16, 1985.

Rept. No. 17 A Versatile Video Tape for Storage and Selective Retrieval of Ion Images for Digital Acquisition and Processing - J.T. Brenna, M.G. Moran, G.H. Morrison, February 7, 1986.

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Rept. No. 19 High Resolution Imaging with the Stigmatic Ion Mictoscope - M.T. Bernius, Y-C Ling, G.H. Morrison, September 15, 1986.

Rept. No. 20 Ionization Probability Variations Due to Matrix in Ion Microscopic Analysis of Plastic-Embedded and Ashed Biological Specimens - J.T. Brenna, G.H. Morrison, October 1, 1986.

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